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Metallurgical Calculations: Smelting of copper ores

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Metallurgical Calculations.

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Smelting of Copper Ores.

The smelting down to matte is done either in reverberatory furnaces or in shaft furnaces. The charges are usually composed of roasted ore, roasted matte or speiss, mixed with unroasted sulphides, usually concentrates, and with siliceous rock or limestone as flux. The important reaction during the smelting down is the formation of Cu^2S by the copper present, the formation of other sulphides, mostly FeS, by the larger part of the sulphur left over, and the slagging of the elements which do not enter the matte. If much lead is present metallic lead will separate out, carrying the bulk of the precious metals, but this phenomenon will be considered under the metallurgy of lead. The important subjects for calculation are: the proportions of roasted and unroasted materials to be used, and the proportions of flux to use to make a satisfactory slag.

Some data of importance for calculations on copper smelting have been determined in the author's laboratory by Mr. Walter S. Landis.

A copper matte containing 47.3 copper, 26.2 iron and 23.6 sulphur, was found to have the following thermo-physical characteristics:

Melting point		1,000° C.
Mean specific heat, $o - t = Sm$	$= 0.21104 - 0.0000366\,t$	
Actual specific heat, at $t = S$	$= 0.21104 - 0.0000732\,t$	
Heat content, solid, at 1,000°	=	174 Cal.
Heat content, liquid, at 1,000°	=	204 "
Latent heat of fusion, at 1,000°	=	30 "
Specific heat, at 1,000°	=	0.138

Heat of formation from Cu^2S and FeS not satisfactorily determined.

A copper blast furnace slag containing 35.5 SiO^2, 39.7 FeO, 1.0 MnO, 11.4 CaO, 2.7 MgO, 9.2 Al^2O^3, 0.42 Cu, 0.42 S, was found to have the following characteristics:

Melting point		1,114° C.
Mean specific heat, $o - t = Sm$	$= 0.20185 + 0.0000302\,t$	
Actual specific heat, at $t = S$	$= 0.20185 + 0.0000604\,t$	
Heat content, solid, at 1,114°	=	262 Cal.
Heat content, liquid, at 1,114°	=	302 "
Latent heat of fusion, at 1,114°	=	40 "
Specific heat, at 1,114°	=	0.269

Heat of formation from its constituent oxides = 133 Calories per kg. of slag.

In the case of the slag, its melting point and latent heat of fusion are not nearly as sharply defined as those of the matte, since the matte melts sharply, but the slag goes through a pasty or viscous stage. The values given are the best approximations which could be gotten from the experiments. As regards heat of formation, the constituent oxides were carefully weighed, mixed with a known weight of carbon, and ignited in a Berthelot bomb calorimeter. Several experiments gave satisfactory concordant results, so that the heat of combination of the constituents of this slag may be taken as not far from 133 Calories per kilo. of slag. By following this scheme it is possible to measure experimentally the heat of formation of any slag whose analysis is known.

Reverberatory Smelting.

In the reverberatory furnace the atmosphere is in no case strongly reducing; it may be varied from weakly reducing to strongly oxidizing, and in the smelting operation usually averages about neutral. The consequence of this is that copper oxides or sulphate in the charge are not deoxidized by carbon, as in the shaft furnace, nor is Fe^2O^3 reduced to FeO by carbon, but the oxygen thus contained in the charge largely goes off with sulphur as SO^2, thus decreasing the amount of sulphur left to form matte, and therefore increasing the percentage of copper in the matte formed. The reactions are mainly:

$$2CuO + 2FeS + 2Fe^2O^3 + 6SiO^2 = SO^2 + Cu^2S + 6FeSiO^3.$$

The slag $FeSiO^3$ is, however, heavy and viscous; it would contain 45 per cent of silica, but runs better and gives a cleaner separation from matte if some lime is added to it. The replacement of 10 per cent of FeO in this silicate by 10 per cent of CaO lowers its melting point from 1,110° C. to 1,010°, and therefore makes a slag that is much easier to keep fluid and of greater fluidity at any given furnace temperature.

Problem 105.

Peter's (*Modern Copper Smelting*, p. 446) gives the composition of the average mixture smelted in the reverberatory furnaces at Argo, Col., as

	Per Cent.
SiO^2	33.9
Iron	10.8
$BaSO^4$	15.5
Al^2O^3	5.6
$CaCO^3$	8.5
$MgCO^3$	5.8
ZnO	6.1
Copper	2.0
Sulphur	5.1
Oxygen	6.4
	99.7

The furnace smelts 50 tons of this mixture (charged hot, at 350° C.) in 24 hours, using 13.5 tons of bituminous coal and producing a matte with 40 per cent of copper. Outside dimensions of furnace 20 x 40 x 6 feet. Area of stack, fire-box and hearth 16, 32.5 and 481 square feet, respectively. Temperature of stack gases 1,000° C. Composition of the coal: moisture 1.40 per cent, fixed carbon 54.90, volatile matter 32.90, ash 10.80 per cent; assume 10 per cent more air used than necessary for theoretical combustion. Temperature of slag and matte 1,200°.

Required:

(1) The weight of matte produced, assuming the slag to carry 0.2 per cent of copper (as intermingled matte), and the matte 40 per cent.

(2) The loss of copper in the slag, expressed in per cent of the total copper present.

(3) The percentage of the calorific power of the fuel existing in the stack gases, the slag and the matte.

(4) The heat lost by radiation and conduction in pound Calories per minute per square foot of furnace surface.

(5) The velocity of the hot gases at the base of the stack.

(6) The horse-power theoretically obtainable by passing the hot gases through a boiler which reduces their temperature to 200° C., and which, together with the steam engine gives a total thermomechanical efficiency of 7.5 per cent upon the heat furnished to (entering) the boiler.

Solution:

(1) The entire matte formed, that free plus that intermingled with the slag, will be per 100 of ore mixture

$$2.0 \div 0.40 = 5.0 \text{ pounds.}$$

	Pounds.
FeS in this matte $= 5.0 - 2.5$	= 2.5
Fe in this matte $= 2.5 \times 56/88$	= 1.6
Fe going to slag as FeO $= 10.8 - 1.6$	= 9.2
FeO in slag $= 9.2 \times 72/56$	= 11.8
Constituents of slag:	
SiO^2	= 33.9
FeO	= 11.8
$BaO = 15.5 \times 153/233$	= 5.9
Al^2O^3	= 5.6
$CaO = 8.5 \times 56/100$	= 4.8

$MgO = 5.8 \times 40/84$	=	2.8
ZnO	=	6.1
Weight of slag	=	70.9
Copper in slag as intermingled matte	=	0.14
Intermingled matte lost in slag	=	0.35
Free matte obtained = 5.0 — 0.35	=	**4.65** (1)

(2) $$\frac{0.14}{2.00} = 0.07 = 7 \text{ per cent.} \qquad (2)$$

(3) The calorific power of the fuel may be calculated from its proximate analysis by the method of Goutal (ELECTROCHEMICAL AND METALLURGICAL INDUSTRY, April, 1907, p. 145), as follows:

Pure fuel 1.0000 — 0.1220	=	0.8780
Per cent of this volatile $\frac{0.3290}{0.8780}$	=	37.5 per cent.
Calorific power of volatile matter	=	8,650 Cal.
Calorific power (to liquid H^2O):		
Carbon 0.5490 × 8,100	=	4,447 "
Vol. matter 0.3290 × 8,650	=	2,846 "
Sum	=	7,293 "
Water formed = 0.45		
Latent heat of vaporization of water = 0.45 × 606.5	=	273 "
Metallurgical calorific power	=	7,020 "

Assuming the volatile matter to be 15 per cent hydrogen, 40 per cent oxygen and 45 per cent carbon, the coal contains:

Hydrogen	0.329 × 0.15	= 0.049
Volatile carbon	0.329 × 0.45	= 0.148
Fixed carbon		= 0.549
Total carbon		= 0.697

and the air necessary for combustion and products therefrom are per unit weight of fuel used:

Oxygen for C = 0.697 × 8/3	=	1.859 pounds.
Oxygen for H = 0.049 × 8	=	0.392 "
Sum	=	2.251 "
Oxygen in coal = 0.329 × 0.40	=	0.132 "
Oxygen needed from air	=	2.119 "
Air needed = $\frac{2.119 \times 13/3 \times 16}{1.293}$	=	113.7 ft³.
Nitrogen therein = 113.7 × 0.792	=	90.0 "
10 per cent surplus air	=	11.4 "
Volume of CO^2 = $\frac{2.556 \times 16}{1.98}$	=	20.7 "
Volume of H^2O = $\frac{0.455 \times 16}{0.81}$	=	9.0 "

Assuming the tons mentioned are of 2,000 pounds each, the heat generated per 27,000 pounds of fuel used per day is

$$27{,}000 \times 7{,}020 = 189{,}540{,}000 \text{ pound Calories,}$$

and, therefore, per 100 pounds of ore smelted:

$$189{,}540{,}000 \div 1{,}000 = 189{,}540 \text{ pound Calories.}$$

The fuel used per 100 pounds of ore being 54 pounds, the products of combustion are 54 times the above calculated volumes, to which must be added

7.4 pounds $SO^2 = (7.4 \times 16) \div 2.88 = 41$ cubic feet.
6.0 pounds $SO^3 = (6.0 \times 16) \div 3.60 = 27$ " "
6.7 pounds $SO^2 = (6.7 \times 16) \div 1.98 = 54$ " "

found later to be driven off the charge. The stack gases and the heat carried out by them are as follows:

CO^2	613 × 0.59 × 1,000	=	361,670 ounce Cal.
H^2O	243 × 0.49 × 1,000	=	119,070 " "
N^2 Air	2,738 × 0.33 × 1,000	=	903,540 " "
SO^2	41 × 0.66 × 1,000	=	27,060 " "
SO^3	27 × 0.58 × 1,000	=	15,660 " "
			1,427,000 " "
		=	89,200 pound Cal.

Proportion of the calorific power of the fuel in the hot gases:

$$\frac{89{,}200}{189{,}540} = 0.47 = \mathbf{47} \text{ per cent.} \qquad (3)$$

To find the heat in the slag tapped, taking Landis's determination of 302 Calories in slag melted at its melting point, 1,114°, and assuming a specific heat in the melted state of 0.27, we have the heat in it per unit weight at 1,200°:

$$302 + (0.27 \times 86) = 325 \text{ Cal.}$$

Heat in total slag:

$$325 \times 70.9 = 23{,}045 \text{ Cal.}$$

Proportion of calorific power of fuel in hot slag:

$$\frac{23.045}{189{,}540} = 0.121 = \mathbf{12.1} \text{ per cent.} \qquad (3)$$

To find the heat in the matte, we may take Landis's determination of 204 Calories in matte just melted at 1,000°, and assuming a specific heat of 0.14 we have heat in unit weight at 1,200°:

$$204 + (0.14 \times 200) = 232 \text{ Cal.}$$

And, therefore, heat in the matte formed:

$$4.65 \times 232 = 1{,}080 \text{ Cal.}$$

Proportion of calorific power of fuel in melted matte:

$$\frac{1{,}080}{189{,}540} = 0.006 = \mathbf{0.6} \text{ per cent.} \qquad (3)$$

(4) The heat lost by radiation and conduction equals all the heat brought in and generated by combustion and other chemical reactions in the furnace, minus that absorbed by chemical reactions in the furnace, and minus that issuing as sensible heat in the stack gases, slag and matte. The ore mixture being charged hot, at 350° C., and having an assumed specific heat of 0.15, its sensible heat is

	Calories.
100 × 0.15 × 350 =	5,250
Add heat of combustion of coal =	189,540
Heat available =	194,790

The heats of chemical reaction of sulphates and oxides on sulphides are quite complex, and we will show the calculation in detail at the end of the problem. Suffice here to give the end results of the calculation:

	Calories.
Chemical reactions, net *absorption*	16,480
Heat of formation of slag, *evolved*	+ 9,430
Net heat *absorbed* in reactions and combinations	7,050

The heat balance sheet will therefore show:

Available.

	Calories.
Heat in hot charges	5,250
Heat of combustion of coal	189,540
	194,790

Distribution.

In chimney gases	89,200
In liquid slag, tapped out	23,045

In liquid matte, tapped out.....	1,080
Absorbed in reactions and combinations	7,050
Loss by radiation and conduction.....	74,425
	194,790

The loss by radiation and conduction per day will be:

		Calories.
	74,425 × 270	= 20,093,000
per minute	20,093,000 ÷ 1,440	= 14,000

The whole outside area of the furnace, including the base, is

$$2(20 \times 40) + 2(6 \times 40) + 2(6 \times 20) = 2{,}320 \text{ sq. ft.}$$

Loss in pound Calories per square foot of surface per minute:

$$14{,}000 \div 2{,}320 = \mathbf{6.0} \text{ pound Cal.}$$

(5) The volume of stack gases, at 0° C., has been found to be 3,662 cubic feet per 100 pounds of fuel used, or $3{,}662 \times 270 = 988{,}740$ cubic feet per day = 11.4 cubic feet per second. At 1,000° this volume would be

$$11.4 \times (1{,}000 + 273) \div 273 = 53.2 \text{ cubic feet.}$$

And since the area of stack cross-section is 16 square feet the velocity of the hot gases entering the stack is

$$53.2 \div 16 = \mathbf{3.3} \text{ feet per second.} \qquad (5)$$

This is a low velocity, and shows good design, which will result in better economy of fuel than if high velocity were used.

(6) The gases were found to contain 89,200 pound Cal. per 100 of ore smelted, or per day:

$$89{,}200 \times 1{,}000 = 89{,}200{,}000 \text{ pound Cal.}$$

per hour = 3,717,000 " "

Since 1 hp. equals 1,400 pound Cal. per hour, we have:

Horse-power at 100 per cent efficiency:

$$3{,}717{,}000 \div 1{,}400 = 2{,}650$$

Horse-power at 7.5 per cent efficiency:

$$2{,}650 \times 0.075 = \mathbf{199} \text{ H. P.} \qquad (6)$$

In connection with requirement (3) of above problem it will be interesting and instructive to discuss the chemical and especially the thermochemical phenomena accompanying the smelting down of the ore mixture. The discussion will be clearest if we take the actual figures of the problem in question.

Aside from the SiO^2, Al^2O^3, etc., the ore mixture contains

	Per Cent.
Fe	10.8
Cu	2.0
S	5.1
O	6.4

And these four ingredients are present either as FeS, FeO, Fe^2O^3, $FeSO^4$, Cu^2S, Cu^2O, CuO or $CuSO^4$. With the above quantities of the four elements in question, however, the manner in which they are combined is fixed within rather narrow limits. Each of the four binds each of the others, and it can be found, by some patience and trying out, that the four elements, constituting 23.4 per cent of the ore mixture, must be combined about as follows in order to be present in the quantities given:

	Per Cent.
CuO	1.0
$CuSO^4$	3.0
FeS	7.3
$FeSO^4$	8.9
FeO	0.4
Fe^2O^3	3.7

The best proof of this statement is to resolve the weights of these compounds into their components, and to thus prove that they agree with the premises.

On melting this down to 40 per cent matte we produce

Cu^2S	2.5 per cent in matte.
FeS	2.5 per cent in matte.
SO^2	7.4 per cent in gases.
FeO	11.8 per cent to slag.

The heat represented by the formation of the products must be subtracted from the heat of formation of the materials reacting to get the net heat of the reaction. We will multiply the amount of each material by the heat of formation of unit weight from its elements as follows:

				Cal.
CuO	1.0 × (37,700 ÷ 79.6)	= 1.0 ×	473 =	473
$CuSO^4$	3.0 × (181,700 ÷ 159.6)	= 3.0 ×	1,139 =	3,417
FeS	7.3 × (24,000 ÷ 88)	= 7.3 ×	273 =	1.993
$FeSO^4$	8.9 × (214,500 ÷ 152)	= 8.9 ×	1,411 =	12,558
FeO	0.4 × (65,700 ÷ 72)	= 0.4 ×	913 =	365
Fe^2O^3	3.7 × (195,600 ÷ 160)	= 3.7 ×	1,223 =	4,525
			Sum =	23,331

Heat of formation of products:

Cu^2S	2.5 × (20,300 ÷ 159)	= 2.5 ×	128 =	320
FeS	2.5 × (24,000 ÷ 88)	= 2.5 ×	273 =	683
SO^2	7.4 × (69,260 ÷ 64)	= 7.4 ×	1,082 =	8,007
FeO	11.8 × (65,700 ÷ 72)	= 11.8 ×	913 =	10,773
			Sum =	19,782
			Difference, heat absorbed =	3,549

We have, therefore, a deficit, or heat to be supplied. This deficit is increased by the heat required to decompose $BaSO^4$ into BaO and SO^3, $CaCO^3$ into CaO and CO^2 and $MgCO^3$ into MgO and SO^2; while it is decreased by the heat of combination of Cu^2S and FeS to form matte, and the heat of combination of SiO^2 with BaO, Al^2O^3, CaO, MgO, ZnO and FeO to form slag.

The driving off of SO^3 and CO^2 absorbs

		Calories.
SO^3 from BaO, SO^3	6.0 × 1,189 =	7,134
CO^2 from CaO, CO^2	3.7 × 1,026 =	3,796
CO^2 from MgO, CO^2	3.0 × 666 =	1,998
	Sum =	12,928

The net result of all these reactions, leaving out the formation heat of the slag from its oxide constituents, is

		Lb. Cal.
Absorbed	23.331 + 12,928 =	36,260
Evolved		19,780
Deficit		16,480

And even if we credit the heat of formation of the slag:

	Lb. Cal.
70.9 × 133	= 9,430

there remains a net deficit of 7,050

The reaction of the ore mixture to form matte and slag is therefore an endothermic operation, in spite of the fact that much sulphur goes off as SO^2. The prime reason for this is that the bulk of the sulphur in the roasted ore was present as sulphate and not as sulphide.

Problem 106.

A copper blast furnace has at its disposal materials of the following compositions in percentages:

	Cu.	*Fe.*	*S.*	*SiO^2.*
Selected raw ore....	15	20	35	25
Roasted concentrates	25	35	10	12
Refinery slag.....	50	10	—	25
Limestone	CaO — 50			1

It is desired to make a matte with 50 per cent copper and a slag containing 35 per cent SiO^2, 40 per cent FeO and 15 per cent CaO, or with these ingredients in those proportions.

Required:

(1) The proportions of charge.

(2) A balance sheet showing distribution of these materials.

Solution: The foregoing conditions are those which frequently confront the copper smelter. He has at hand raw ore and roasted concentrates, whose relative quantities he can usually vary at will by simply concentrating and roasting more or less material. He has return slags from the refinery furnaces which, however, are not unlimited in quantity but bear a general relation to the weight of matte made and sent on to the further operations. Finally, the limestone can be varied at will. It will readily be seen that if the charge is fixed at a certain quantity of raw ore to start with, that there are then three variables, the quantities of the other three materials, and to fix these there are practically only two conditions to be fulfilled, the two ratios between three components of the slag. In order to make a practical solution, it is necessary to make an assumption which will practically reduce the number of variables by one, and on looking over the ground it is seen that the most rational assumption which can be made is to assume the refinery slag to bear a given relation to the weight of matte produced. Such an assumption eliminates the weight of refinery slag as a variable, and leaves us with only two variables and two conditions to fill, which makes a solution possible. Assuming the charges to be based on 100 of roasted ore, we can call the weight of roasted concentrate used X, the weight of refinery slag Y, and the weight of limestone Z, and then figure out the weight of matte produced in terms of X, Y and Z. Assuming then that the refinery slag is, say, 0.25 of the weight of matte, we have $Y = \frac{1}{4}$ (expression for weight of matte), and thus one equation between X Y and Z. The ingredients of the slag being figured out in terms of X, Y and Z, the assumed relations between FeO, CaO and SiO^2 in the slag give us two more equations between X, Y and Z, and thus all three quantities can be determined.

The provisional balance sheet, based on 100 of ore and X, Y and Z of other ingredients of the charge, will be as follows:

BALANCE SHEET.

Ore.	(100).	*Matte.*	*Slag.*
Cu	15	Cu 15	
Fe	20	Fe 7.2 + 0.14Y	FeO 16.5 — 0.18Y
S	35	S 7.8 + 0.03X + 0.26Y	
SiO^2	25		SiO^2 25.0
R'st'd Conc.	(X).		
Cu	0.25X	Cu 0.25X	
Fe	0.35X	Fe 0.12X	FeO 0.30X
S	0.10X	S 0.10X	
SiO^2	0.12X		SiO^2 0.12X 12
Ref. Slag.	(Y).		
Cu	0.50Y	Cu 0.50Y	
Fe	0.10Y	Fe 0.10Y	
SiO^2	0.25Y		SiO^2 0.25Y
Lime-stone.	(Z).		
CaO	0.50Z		CaO 0.50Z
SiO^2	0.01Z		SiO^2 0.01Z

Notes on above balance sheet:

Copper in the matte	15	+ 0.25 X + 0.50 Y
Weight of matte (50 per cent Cu)	30	+ 0.50 X + 1.00 Y
Weight of S in matte	7.8	+ 0.13 X + 0.26 Y
Weight of Fe in matte	7.2	+ 0.12 X + 0.24 Y

These weights of S and Fe are therefore provided for under the column "matte," taking them from the various materials charged.

The refinery slag being assumed 0.25 of the matte, we have at once

$$Y = 0.25\ (30 + 0.50\,X + 1.00\,Y)$$
$$= 7.5 + 0.13\,X + 0.25\,Y$$

whence $Y = 10 + 0.17\,X$

That is, the refinery slag equals in weight 0.1 the ore plus 0.17 the roasted concentrates. This practically amounts to leaving the roasted concentrates and limestone as the only variables.

The problem can now be solved by summing up the ingredients of the slag as follows:

$$FeO = 16.5 - 0.18\,Y + 0.30\,X$$
$$SiO^2 = 25.0 + 0.25\,Y + 0.12\,X + 0.01\,Z$$
$$CaO = 0.5\,Z$$

or substituting $Y = 10 + 0.17\,X$

$$FeO = 14.7 + 0.27\,X$$
$$SiO^2 = 27.5 + 0.16\,X + 0.01\,Z$$
$$CaO = 0.5\,Z$$

And since the requirements of the slag are that

$$SiO^2 = \frac{35}{40}\,FeO$$

and

$$CaO = \frac{15}{40}\,FeO$$

we have:

$$27.5 + 0.16\,X + 0.01\,Z = \frac{35}{40}\,(14.7 + 0.27\,X)$$

$$0.50\,Z = \frac{15}{40}\,(14.7 + 0.27\,X)$$

whence

$$X = 195 \quad Z = 48$$

and, therefore, $Y = 43$

The final balance sheet then becomes:

BALANCE SHEET.

Ore.	(100).	*Matte.*	*Slag.*
Cu	15	Cu 15	
Fe	20	Fe 20	
S	35	S 35	
SiO^2	25		SiO^2 25
Rs'l'd Conc.	(195).		
Cu	49	Cu 49	
Fe	68	Fe 17	FeO 66
S	20	S 10	
SiO^2	23		SiO^2 23
Ref. Slag.	(43.)		
Cu	22	Cu 22	
Fe	4	Fe 4	
SiO^2	11		SiO^2 11
Limestone.	(48).		
CaO	24		CaO 24
SiO^2	1		SiO^2 1
		172	150

Matte.	*Per Cent.*	*Slag.*	*Ratio.*
Cu	86 = 50	SiO^2	60 = 36
Fe	41 = 24	FeO	66 = 40
S	45 = 26	CaO	24 = 14
	172		150 90

Furnace managers are usually afraid of X, Y and Z, and in regular running there is usually little need for an algebraic solution, yet many occasions arise when a judicious use of algebra solves a problem in an exact manner which hardly any amount of guessing or approximating can attain efficiently. In bringing forward this solution we may lay ourselves open to being called pedantic or academic, but the fact is that *the conditions of this problem* were proposed to the writer as a difficult nut to crack by a practical copper smelter, and the algebraic solution furnished was characterized by him as the most satisfactory solution of this class of problems which he had yet seen.